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FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER
IN-5550

U.S. APPLICATION NO. (IF KNOWN SEE 37 RR 15)
10/030307

INTERNATIONAL APPLICATION NO.
PCT/EP00/06286

INTERNATIONAL FILING DATE
5 July 2000 (5.7.2000)

PRIORITY DATE CLAIMED
12 July 1999 (12.07.1999)

TITLE OF INVENTION: **AQUEOUS COATING SUBSTANCE, METHOD FOR ITS PRODUCTION AND ITS USE**

APPLICATION(S) FOR DO/EO/US: **Lutz-Werner GROSS, Ludwig MOORKAMP, Heinz-Ulrich GRUMPE, and Ulrich POTH**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

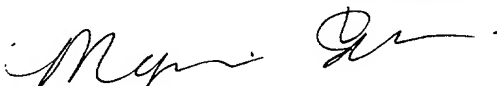
1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:

**A copy of the cover sheet from the PCT Published Application
Cover Page of Priority Document**

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. **ET332278329US** addressed to the Commissioner for Patents, Washington, D.C. 20231 on January 4, 2002.



Marjorie Ellis

| | | | | | |
|---|--------------|--|------------|--|--|
| U.S. APPLICATION NO. (If known see 37 C.F.R. 1.50) 10/030307 | | INTERNATIONAL APPLICATION NO. PCT/EP00/06286 | | ATTORNEY'S DOCKET NUMBER IN-5550 | |
| 17: <input checked="" type="checkbox"/> The following fees are submitted | | | | CALCULATIONS PTO USE ONLY | |
| Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... | | | | \$970.00 | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... | | | | \$890.00 | |
| International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.44(a)(2)) paid to USPTO..... | | | | \$690.00 | |
| International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)..... | | | | \$670.00 | |
| International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) | | | | \$ 96.00 | |
| ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | \$890.00 | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$130.00 | |
| Claims | Number Filed | Number Extra | Rate | | |
| Total Claims | 38 - 20 = | 18 | X \$18.00 | \$324.00 | |
| Independent claims | 03 - 03 = | 0 | X \$80.00 | \$ | |
| Multiple dependent claims(s) (if applicable) | | | + \$270.00 | \$ | |
| TOTAL OF ABOVE CALCULATION = | | | | \$1,344.00 | |
| Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). | | | | \$ | |
| SUBTOTAL = | | | | \$1,344.00 | |
| Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | + | |
| TOTAL NATIONAL FEE = | | | | \$1,344.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + | | | | \$ | |
| TOTAL FEES ENCLOSED = | | | | \$1,344.00 | |
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- a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 23-3425 in the amount of \$1,344.00 to cover the above fees
A triplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 23-3425. A triplicate copy of this sheet is enclosed.
appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR
1.137(a) or (b)) may be filed and granted to restore the application to pending status.

INDENCE TO:
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Michael F. Morgan

Name

42,906

REGISTRATION NUMBER

FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

| | | |
|--|--|---|
| ATTORNEY DOCKET NUMBER IN-5550 | U.S. APPLICATION NO. (IF KNOWN SEE 37 RR 15) 10/030307 | |
| INTERNATIONAL APPLICATION NO. PCT/EP00/06286 | INTERNATIONAL FILING DATE 5 July 2000 (5.7.2000) | PRIORITY DATE CLAIMED 12 July 1999 (12.07.1999) |

TITLE OF INVENTION: **AQUEOUS COATING SUBSTANCE, METHOD FOR ITS PRODUCTION AND ITS USE**

APPLICATION(S) FOR DO/EO/US: **Lutz-Werner GROSS, Ludwig MOORKAMP, Heinz-Ulrich GRUMPE, and Ulrich POTH**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

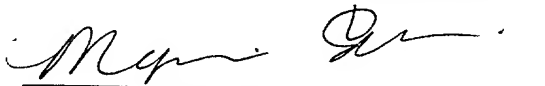
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8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
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Marjorie Ellis

PATENT
(Practitioner's Docket No. IN-5550)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Lutz-Werner GROSS
Ludwig MOORKAMP
Heinz-Ulrich GRUMPE
Ulrich POTH

Serial No.: This application is a National
Phase of Patent Application PCT/EP00/06286
filed 05 July 2000.

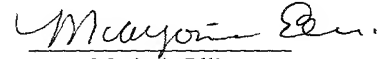
Filed: January 4, 2002

For: AQUEOUS COATING SUBSTANCE,
METHOD FOR ITS PRODUCTION AND
ITS USE

Group Art Unit: Not Assigned

Examiner: Not Assigned

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being deposited with the United States Postal Service in an
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Label No. **ET332278329US** addressed to Box Patent
Application Commissioner for Patents, Washington, D.C.
20231 on January 4, 2002.


Marjorie Ellis

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115

Box Patent Application
Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

This preliminary amendment is submitted with the application for entry into the U.S.
National Phase under Chapter II. This application is based on PCT/EP00/06286 filed on 5
July 2000.

In connection with the filing of this National Phase application, please make the
following preliminary amendments.

IN THE SPECIFICATION

After the title, please insert --This application is a National Phase Application of
Patent Application **PCT/EP00/06286** filed on 5 July 2000.--

In the abstract on pages 92 and 93, please substitute the following abstract. A marked copy showing changes to the abstract is listed below.

(Amended) An aqueous coating material comprising

- A) at least one polyester that is water-soluble or water-dispersible,
- B) at least one polyurethane acrylate that is water-soluble or water-dispersible,
- C) at least one amino resin that is itself water-soluble or water-dispersible or is water-soluble or water-dispersible in the presence of the polyester and the polyurethane acrylate,
- D) at least one of a color pigment, an effect pigment, a color and effect pigment, and a filler, and
- E) optionally at least one polyisocyanate.

Also, processes for preparing and using the aqueous coating material.

IN THE CLAIMS:

Please cancel claims 1-16 without prejudice or disclaimer.

Please add claims 17-54.

17. (New) An aqueous coating material comprising

- A) at least one polyester that is water-soluble or water-dispersible,
- B) at least one polyurethane acrylate that is water-soluble or water-dispersible,
- C) at least one amino resin that is itself water-soluble or water-dispersible or is water-soluble or water-dispersible in the presence of the polyester and the polyurethane acrylate,
- D) at least one of a color pigment, an effect pigment, a color and effect pigment, and a filler, and
- E) optionally, at least one polyisocyanate,

wherein the polyester comprises a reaction product of

a1) a mixture comprising

- a11) from 40 to 80 mol% of at least one of an aliphatic polycarboxylic acid, a cycloaliphatic polycarboxylic acid, an esterifiable derivative of an aliphatic polycarboxylic acid, and an esterifiable derivative of a cycloaliphatic polycarboxylic acid,

a12) from 20 to 60 mol% of at least one of an aromatic polycarboxylic acid and an esterifiable derivative of an aromatic polycarboxylic acid;

and

a2) at least 60 mol% of at least one of an aliphatic polyol and a cycloaliphatic polyol, wherein each of the aliphatic polyol and the cycloaliphatic polyol include in its molecule at least one structural element $-C(R^1R^2)-CH_2OH$, wherein R^1 and R^2 are each at least one of a methylol group, a 1 to 20 carbon aliphatic hydrocarbon radical, a cyclo-aliphatic hydrocarbon radical, and an aromatic hydrocarbon radical.

18. (New) The coating material of claim 17, wherein a1) and a2) are reacted with one another in a molar ratio a1):a2) of 1.1:1 to 2:1.
19. (New) The coating material of claim 17, wherein the degree of branching of the polyester is from 1.0 to 2.0 mol/kg.
20. (New) The coating material of claim 17, wherein the polyester has at least one of a number-average molecular weight of from 650 to 2500 daltons, an acid number of from 25 to 55 mg KOH/g, and a hydroxyl number of from 80 to 180 mg KOH/g.
21. (New) The coating material of claim 17, wherein the coating material comprises a mixture product of
- A) from 2 to 90% by weight of the polyester,
 - B) from 1 to 80% by weight of the polyurethane acrylate,
 - C) from 1 to 80% by weight of the amino resin, and
 - D) from 1 to 95% by weight of at least one of the color pigment, the effect pigment, the color and effect pigment, and the filler,
- the percentages by weight being based on an overall solids content of the coating material.
22. (New) The coating material of claim 17, wherein the polyisocyanate is added in an amount of from 0.5 to 50% by weight based on an overall solids content of the coating material.

23. (New) The coating material of claim 17, wherein (A), (B), and (C) are added in a ratio (A):(B):(C) of 25-70:10-40:10-40.

24. (New) The coating material of claim 17, wherein the polyurethane acrylate comprises a reaction product of a free-radical polymerization in an aqueous dispersion

B1) of at least one dispersed polyurethane resin comprising a reaction product of

b1) at least one polyisocyanate and optionally at least one monoisocyanate;

b2) at least one of a polyesterpolyol and a polyetherpolyol each having a number-average molecular weight of from 400 to 5000;

b3) at least one compound comprising at least one of

b31) at least one isocyanate-reactive group and

b32) at least one of an anionic group and a group convertible into anions by neutralizing agents,

and

b33) at least one nonionic hydrophilic group;

and

b4) at least one compound comprising

b41) at least one isocyanate-reactive group and

b42) at least one olefinically unsaturated group;

and

B2) at least one olefinically unsaturated monomer.

25. (New) The coating material of claim 17, wherein the amino resin comprises a melamine-formaldehyde resin containing C₁ to C₄ alkyl ether groups and containing from 0.1 to 1.5 free imino groups per melamine nucleus.

26. (New) The coating material of claim 17 further comprising at least one ingredient curable with actinic radiation.

27. (New) A process comprising applying the coating material of claim 17 to a substrate to form an at least one coat paint system.

28. (New) The paint system produced by the process of claim 27.
29. (New) A product produced by the process of claim 27.
30. (New) A process for preparing an aqueous coating material comprising mixing at least the following in an aqueous medium:
- A) at least one polyester that is water-soluble or water-dispersible,
 - B) at least one polyurethane acrylate that is water-soluble or water-dispersible,
 - C) at least one amino resin that is itself water-soluble or water-dispersible or is water-soluble or water-dispersible in the presence of the polyester and the polyurethane acrylate, and
 - D) at least one of a color pigment, an effect pigment, a color and effect pigment, and a filler,
- wherein the polyester comprises a reaction product of
- a1) a mixture comprising
 - a11) from 40 to 80 mol% of at least one of an aliphatic polycarboxylic acid, a cycloaliphatic polycarboxylic acid, an esterifiable derivative of an aliphatic polycarboxylic acid, and an esterifiable derivative of a cycloaliphatic polycarboxylic acid,
 - a12) from 20 to 60 mol% of at least one of an aromatic polycarboxylic acid and an esterifiable derivative of an aromatic polycarboxylic acid;
- and
- a2) at least 60 mol% of at least one of an aliphatic polyol and a cycloaliphatic polyol, wherein each of the aliphatic polyol and the cycloaliphatic polyol include in its molecule at least one structural element $-C(R^1R^2)-CH_2OH$, wherein R^1 and R^2 are each at least one of a methylol group, a 1 to 20 carbon aliphatic hydrocarbon radical, a cyclo-aliphatic hydrocarbon radical, and an aromatic hydrocarbon radical.
31. (New) The process of claim 30, wherein a1) and a2) are reacted with one another in a molar ratio a1):a2) of 1.1:1 to 2:1.

32. (New) The process of claim 30, wherein the degree of branching of the polyester is from 1.0 to 2.0 mol/kg.
33. (New) The process of claim 30, wherein the polyester has at least one of a number-average molecular weight of from 650 to 2500 daltons, an acid number of from 25 to 55 mg KOH/g, and a hydroxyl number of from 80 to 180 mg KOH/g.
34. (New) The process of claim 30, wherein the coating material comprises a mixture product of
- A) from 2 to 90% by weight of the polyester,
 - B) from 1 to 80% by weight of the polyurethane acrylate,
 - C) from 1 to 80% by weight of the amino resin, and
 - D) from 1 to 95% by weight of at least one of the color pigment, the effect pigment, the color and effect pigment, and the filler,
- the percentages by weight being based on an overall solids content of the coating material.
35. (New) The process of claim 30, wherein (A), (B), and (C) are added in a ratio (A):(B):(C) of 25-70:10-40:10-40.
36. (New) The process of claim 30, wherein the polyurethane acrylate comprises a reaction product of a free-radical polymerization in an aqueous dispersion
- B1) of at least one dispersed polyurethane resin comprising a reaction product of
 - b1) at least one polyisocyanate and optionally at least one monoisocyanate;
 - b2) at least one of a polyesterpolyol and a polyetherpolyol each having a number-average molecular weight of from 400 to 5000;
 - b3) at least one compound comprising at least one of
 - b31) at least one isocyanate-reactive group and
 - b32) at least one of an anionic group and a group convertible into anions by neutralizing agents,and
 - b33) at least one nonionic hydrophilic group;
- and

- b4) at least one compound comprising
 - b41) at least one isocyanate-reactive group and
 - b42) at least one olefinically unsaturated group;

and

- B2) at least one olefinically unsaturated monomer.

37. (New) The process of claim 30, wherein the amino resin comprises a melamine-formaldehyde resin containing C₁ to C₄ alkyl ether groups and containing from 0.1 to 1.5 free imino groups per melamine nucleus.

38. (New) The process of claim 30, wherein the mixing further comprises at least one ingredient curable with actinic radiation.

39. (New) The process of claim 30 further comprising applying the coating material to a substrate to form an at least one coat paint system.

40. (New) The paint system produced by the process of claim 39.

41. (New) A product produced by the process of claim 39.

42. (New) A process for preparing an aqueous coating material comprising

I) mixing at least one of the following in an aqueous medium:

- A) at least one polyester that is water-soluble or water-dispersible,
- B) at least one polyurethane acrylate that is water-soluble or water-dispersible,
- C) at least one amino resin that is itself water-soluble or water-dispersible or is water-soluble or water-dispersible in the presence of the polyester and the polyurethane acrylate, and
- D) at least one of a color pigment, an effect pigment, a color and effect pigment, and a filler,

to give component (I);

and

II) mixing component (I) with at least one polyisocyanate,

wherein the polyester comprises a reaction product of

a1) a mixture comprising

a11) from 40 to 80 mol% of at least one of an aliphatic polycarboxylic acid, a cycloaliphatic polycarboxylic acid, an esterifiable derivative of an aliphatic polycarboxylic acid, and an esterifiable derivative of a cycloaliphatic polycarboxylic acid,

a12) from 20 to 60 mol% of at least one of an aromatic polycarboxylic acid and an esterifiable derivative of an aromatic polycarboxylic acid;

and

a2) at least 60 mol% of at least one of an aliphatic polyol and a cycloaliphatic polyol, wherein each of the aliphatic polyol and the cycloaliphatic polyol include in its molecule at least one structural element $-C(R^1R^2)-CH_2OH$, wherein R^1 and R^2 are each at least one of a methylol group, a 1 to 20 carbon aliphatic hydrocarbon radical, a cyclo-aliphatic hydrocarbon radical, and an aromatic hydrocarbon radical.

43. (New) The process of claim 42, wherein a1) and a2) are reacted with one another in a molar ratio a1):a2) of 1.1:1 to 2:1.

44. (New) The process of claim 42, wherein the degree of branching of the polyester is from 1.0 to 2.0 mol/kg.

45. (New) The process of claim 42, wherein the polyester has at least one of a number-average molecular weight of from 650 to 2500 daltons, an acid number of from 25 to 55 mg KOH/g, and a hydroxyl number of from 80 to 180 mg KOH/g.

46. (New) The process of claim 42, wherein the coating material comprises a mixture product of

A) from 2 to 90% by weight of the polyester,

B) from 1 to 80% by weight of the polyurethane acrylate,

C) from 1 to 80% by weight of the amino resin, and

D) from 1 to 95% by weight of at least one of the color pigment, the effect pigment, the color and effect pigment, and the filler,

the percentages by weight being based on an overall solids content of the coating material.

47. (New) The process of claim 42, wherein the polyisocyanate is added in an amount of from 0.5 to 50% by weight based on an overall solids content of the coating material.
48. (New) The process of claim 42, wherein (A), (B), and (C) are added in a ratio (A):(B):(C) of 25-70:10-40:10-40.
49. (New) The process of claim 42, wherein the polyurethane acrylate comprises a reaction product of a free-radical polymerization in an aqueous dispersion
- B1) of at least one dispersed polyurethane resin comprising a reaction product of
 - b1) at least one polyisocyanate and optionally at least one monoisocyanate;
 - b2) at least one of a polyesterpolyol and a polyetherpolyol each having a number-average molecular weight of from 400 to 5000;
 - b3) at least one compound comprising at least one of
 - b31) at least one isocyanate-reactive group and
 - b32) at least one of an anionic group and a group convertible into anions by neutralizing agents,
 - and
 - b33) at least one nonionic hydrophilic group;
 - and
 - b4) at least one compound comprising
 - b41) at least one isocyanate-reactive group and
 - b42) at least one olefinically unsaturated group;
 - and
 - B2) at least one olefinically unsaturated monomer.
50. (New) The process of claim 42, wherein the amino resin comprises a melamine-formaldehyde resin containing C₁ to C₄ alkyl ether groups and containing from 0.1 to 1.5 free imino groups per melamine nucleus.

51. (New) The process of claim 42, wherein the mixing further comprises at least one ingredient curable with actinic radiation.
52. (New) The process of claim 42 further comprising applying the coating material to a substrate to form an at least one coat paint system.
53. (New) The paint system produced by the process of claim 52.
54. (New) A product produced by the process of claim 52.

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MARKED COPY OF THE AMENDED ABSTRACT

As is permitted by 37 C.F.R. §1.121(c)(1)(ii), amendments to the claims are shown by an equivalent marking system. Insertions are still shown by underline, and deletions are shown by strikethrough.

(Amended) An aqueous coating material comprising

A) at least one polyester that is water-soluble or water-dispersible ~~polyester, preparable from~~

a1) ~~a mixture comprising~~

a11) ~~from 40 to 80 mol% of at least one aliphatic or cycloaliphatic polycarboxylic acid or at least one esterifiable derivative of an aliphatic or cycloaliphatic polycarboxylic acid or a mixture of at least two of these starting products;~~

a12) ~~from 20 to 60 mol% of at least one aromatic polycarboxylic acid, at least one esterifiable derivative of an aromatic polycarboxylic acid or a mixture of at least two of these starting products;~~

a2) ~~at least 60 mol% of at least one aliphatic or cycloaliphatic polyol whose molecule includes at least one structural element $C(R^1R^2)CH_2OH$ in which the radicals R^1 and R^2 stand for aliphatic, cycloaliphatic or aromatic hydrocarbon radicals having from 1 to 20 carbon atoms or for methylol groups, or a mixture of at least two of these starting products;~~

B) at least one polyurethane acrylate that is water-soluble or water-dispersible ~~polyurethane acrylate,~~

C) at least one amino resin ~~which per se~~ that is itself water-soluble or water-dispersible or is water-soluble or water-dispersible in the presence of ~~ingredients (A) and (B) is water-soluble or dispersible~~ the polyester and the polyurethane acrylate, and

D) at least one of a color pigment, an effect pigment, ~~and/or~~ a color and effect pigment, ~~and/or one~~ a filler, and also, if desired,

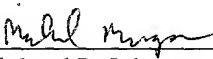
E) optionally at least one polyisocyanate;

~~processes for its preparation, and its use as solid color topecoat material and aqueous basecoat material, especially as a solid color topecoat material for the finishing of commercial vehicle bodies. Also, processes for preparing and using the aqueous coating material.~~

REMARKS

Upon entry of the present amendment claims 17-54 are pending in the application. New claims 17-54 add no new matter, as these claims contain subject matter deleted from the claims 1-16. There are three (3) independent claims and a total of thirty-eight (38) claims pending in the application. The abstract has been amended to conform to the length permitted by the rules. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,



Michael F. Morgan
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Universal pigment pastes and their use for preparing

5 aqueous paints

The present invention has as its subject pigment pastes which comprise as binder at least one polyurethane acrylate (P) that is obtainable by polymerizing, in an
10 organic solvent or in a mixture of organic solvents,

(A) ethylenically unsaturated monomers, or a mixture of ethylenically unsaturated monomers, in the presence of

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(B) a polyurethane resin which has a number-average molecular weight of from 200 to 30,000, preferably from 1000 to 5000, and which contains on average from 0.05 to 1.1, preferably from 0.2 to 0.9 and,
20 with particular preference, from 0.3 to 0.7 polymerizable double bonds per molecule, and converting the resulting reaction product into an aqueous dispersion.

25 The present invention also relates to aqueous coating materials comprising these pigment pastes and to methods of coating substrates. Finally, the invention

relates as well to mixer systems using these pigment pastes.

Aqueous coating materials are pigmented by adding
5 aqueous pigment concentrates, so-called pigment pastes,
to the other constituents of the coating material.

Pigment pastes consist usually of water, at least one
pigment, at least one water-dilutable binder and, if
10 desired, organic solvents, wetting agents and other
additives customary for pigment pastes (cf. Volker
Radke in "Pigmente für Anstrichmittel" [Pigments for
coating materials], Technische Akademie Esslingen, Kap.
7, Dispersion of Pigments, Export-Verlag, 1990).

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In order for these pigment pastes to be able to be used
as universally as possible and so permit the cost-
effective preparation of a large number of in some
cases very different paints, these pigment pastes
20 should be as highly pigmented as possible. However,
this leads in turn generally to a large number of
problems, such as high pigment paste viscosity,
inadequate pigment paste shelf life (in general, the
pigment pastes are desired to have a shelf life of at
25 least 6 months on storage at room temperature or one
month on storage at 40°C) or poor dispersibility (in

other words, a high specific energy input is necessary for dispersing, or the pigment paste thickens in the course of the dispersing operation, or there is a tendency to settling after treatment with a dissolver).

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EP-B-521 928 discloses polyurethane acrylates (P) of the type specified at the outset, and their use for preparing pigment pastes. EP-B-521 928, however, merely describes the preparation of three different basecoats
10 using two different white pastes and one pigment paste containing carbon black. Other pigment pastes are not described in EP-B-521 928.

In addition, EP-B-297 576 discloses aqueous
15 polyurethane resin dispersions which are obtainable by polymerizing ethylenically unsaturated compounds in water in the presence of a polyurethane resin which has no double bonds. These polyurethane resin dispersions can likewise be employed, alone or together with other
20 grinding resins, for grinding pigments in order to prepare aqueous coating materials. In EP-B-297 576, however, it is preferred not to employ, as paste resins, hydroxyl-containing acrylate copolymers prepared in the presence of polyurethanes. Furthermore,
25 the preparation of universal pigment paints is not described in EP-B-297 576.

EP-B-438 090, furthermore, discloses pigment pastes and their use in aqueous coating materials, these pigment pastes comprising a polyester urethane as grinding
5 binder. The use of urethane acrylates as grinding binders, in contrast, is not described in EP-B-438 090. These pigment pastes known from EP-B-438 090 have the disadvantage that the stability of highly pigmented pastes, in respect of viscosity, colour strength and
10 stability of shade in the course of storage of the pigment pastes, is in need of improvement.

In comparison to the pastes known from this EP-B-438 090, the pigment pastes of the present application,
15 despite their high pigment content, are intended to be virtually stable in viscosity on storage of the pastes at room temperature for 6 months; in other words, the viscosity of the pastes after storage remains in the range between 50 and 1000 mPa.s under a shear stress of
20 1000 s⁻¹. In addition, the pigment pastes of the present invention should despite the high pigment content remain stable in terms of colour strength and shade ($\pm 10\%$, $\Delta E \leq 1.5$) on storage of the pastes at room temperature for 6 months.

EP-A-424 705, furthermore, discloses pigment pastes which as grinding binders of a nonionically or partly anionically stabilized dispersion comprise an acrylate/polyurethane graft copolymer. These pigment
5 pastes known from EP-A-424 705 differ from the pigment pastes of the present Application in that the pigment pastes described therein have a low pigment/binder ratio and require long milling periods and/or a high specific energy input ($> 1000 \text{ Wh/kg}$).

10

Finally, EP-A-311 209 discloses universal pigment pastes and their use in mixer systems for preparing aqueous and conventional paints. The pigment pastes described therein and used to prepare aqueous paints
15 comprise from 0 to 65 % by weight of binder, from 10 to 65 % by weight of pigment and also organic solvents and, if desired, further additives. Binders specified for the pigment pastes in EP-A-311 209 are alkyd resins and polyurethane resins. The use of urethane acrylates,
20 on the other hand, is not specified in EP-A-311 209. The pigment pastes in EP-A-311 209 have the disadvantage of a high volatile organic content (VOC).

The object on which the present invention is based,
25 therefore, is to provide aqueous pigment pastes which are universally employable and which are easy and cost-

effective to prepare. In addition, these pigment pastes should meet the usual requirements. They should therefore in particular have a high level of pigmentation and at the same time an adequate shelf life (at least 6 months on storage at room temperature or 1 month on storage at 40°C), good dispersibility (i.e. e.g. required specific energy input 50 - 1000 Wh/kg) and good processability (e.g. pumpability). The pigment pastes should, furthermore, show good formulation and colouristic properties. Finally, the pigment pastes should possess a high colouristic saturation, good colour strength, or good hiding power, and good flow properties.

This object is surprisingly achieved by pigment pastes of the type specified at the outset which are characterized in that they comprise

(Pa) from 10 to 35 % by weight of at least one polyurethane acrylate resin (P), based on the solids content,

(Pb) from 10 to 65 % by weight of water and

(Pc1) from 18 to 40 % by weight of at least one organic, transparent pigment or from 30 to 50 %

by weight of at least one organic, opaque pigment, or

(Pc2) from 30 to 80 % by weight of at least one
5 inorganic pigment, with the exception of white pigments, or from more than 50 to 70 % by weight of white pigment, or

(Pc3) from more than 8 to 15 % by weight of carbon
10 black,

the proportions by weight of the respective components (Pa) to (Pc) being based in each case on the overall weight of the pigment paste.

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Further subjects for the present invention are aqueous paints comprising these pigment pastes, and methods of coating substrates using these paints. Finally, the invention also relates to mixer systems based on these
20 pigment pastes.

It is surprising and was not foreseeable that using the polyurethane acrylates (P) it would be possible to prepare very highly pigmented and yet storage-stable,
25 readily processable pigment pastes which meet the common requirements relating to pigment pastes. Thus it

was not foreseeable that it would even be possible in general to operate with a level of pigmentation in the vicinity of the critical pigment volume concentration (c.p.v.c.). Preferably, the level of pigmentation in
5 this context is generally from about 30 to 10 %, with particular preference from 5 to 7 %, below the c.p.v.c.

Surprisingly, despite the high pigment content, the pigment pastes of the invention even after storage are
10 both virtually stable in viscosity (in other words, the viscosity even after storage at room temperature for 6 months remains at from 50 to 1000 mPa.s at a shear rate of 1000 s⁻¹) and stable in terms of the colour strength and in terms of the shade (i.e. colour strength \pm 10 %,
15 $\Delta E \leq 1.5$).

A further advantage, finally, is that despite the high pigmentation no dispersing problems arise. For example, an energy input of just 50 - 1000 Wh/kg, preferably 100
20 - 400 Wh/kg, is generally sufficient for dispersion. In addition there are generally no problems, for example, such as thickening during the grinding operation or settling after treatment in a dissolver.

In the text below the individual constituents of the pigment paste of the invention will first of all be elucidated further.

5 The polyurethane acrylates (P) employed as binders in the pigment pastes of the invention are known and are described, for example, in EP-B-521 928 on page 2, line 56 to page 8, line 16. For details regarding the preparation of these polyurethane acrylates reference
10 is therefore made to this description in EP-B-521 928.

To prepare the binders (P) employed in accordance with the invention, a polyurethane resin (B) is prepared in a first step in accordance with well-known methods of
15 polyurethane chemistry.

The polyurethane resin is prepared from the following components:

20 (a) a polyester- and/or polyetherpolyol having a number-average molecular weight of from 400 to 5000, or a mixture of such polyester- and/or polyetherpolyols,

(b) a polyisocyanate or a mixture of polyisocyanates,

(c) if desired, a compound which in addition to a polymerizable double bond also contains at least one NCO-reactive group, or a mixture of such compounds,

5 (d) if desired, a compound which in its molecule has at least one isocyanate-reactive group and at least one group which is capable of forming anions, or a mixture of such compounds,

10 (e) if desired, a compound which has in its molecule at least one NCO-reactive group and at least one poly(oxyalkylene) group, or a mixture of such compounds, and, if desired,

15 (f) a hydroxyl- and/or amino-containing organic compound having a molecular weight of from 60 to 600, or a mixture of such compounds.

The polyurethane resin (B) has a number-average
20 molecular weight of from 200 to 30,000, preferably from 1000 to 5000, and contains on average from 0.05 to 1.1, preferably from 0.2 to 0.9 and, with particular preference, from 0.3 to 0.7 polymerizable double bonds per molecule. It is preferred for the polyurethane
25 resin (B) to have an acid number of from 0 to 2.0. The molecular weight of the polyurethane resins can - as

the skilled worker is aware - be controlled in particular by the proportion and functionality of the starting compounds (a) to (f) employed.

- 5 The polyurethane resins (B) can be prepared either in bulk or in organic solvents.

10 The polyurethane resins (B) can be prepared by simultaneous reaction of all starting compounds. In many cases, however, it is judicious to prepare the polyurethane resins in stages. Hence it is possible, for example, to prepare an isocyanate-functional prepolymer from components (a) and (b) which is then reacted further with component (c). It is also possible
15 to prepare, from components (a), (b), (c) and, if used, (d) and (e) an isocyanate-functional prepolymer which can then be reacted with component (f) to give polyurethanes of higher molecular mass. In the cases where use is made as component (c) of a compound which
20 contains only one isocyanate-reactive group, it is possible in a first stage to prepare from (b) and (c) an isocyanate-functional precursor which can subsequently be reacted further with the other components.

The reaction of components (a) to (f) is judiciously carried out in the presence of catalysts such as, for example, dibutyltin dilaurate, dibutyltin maleate, tertiary amines, etc.

5

The amounts of components (a), (b), (c), (d), (e) and (f) to be employed result from the intended number-average molecular weight and the intended acid number. The polymerizable double bonds can be introduced into the polyurethane molecules through the use of components having polymerizable double bonds (a) and/or by way of component (c). It is preferred to introduce the polymerizable double bonds by way of component (c).

15 As component (a) it is possible to employ saturated and unsaturated polyester- and/or polyetherpolyols, especially polyester- and/or polyetherdiols, having a number-average molecular weight of from 400 to 5000. Examples of suitable polyetherdiols are those of the
20 general formula $H(-O-(CHR^1)_n-)_mOH$, where R^1 = hydrogen or a lower, substituted or unsubstituted alkyl radical, $n = 2$ to 6 , preferably 3 to 4 and $m = 2$ to 100 , preferably 5 to 50 . Examples are linear or branched polyetherdiols such as poly(oxyethylene) glycols,
25 poly(oxypropylene) glycols and poly(oxybutylene) glycols.

The polyetherdiols selected should not introduce excessive amounts of ether groups since otherwise the polymers formed swell in water. The preferred
5 polyetherdiols are poly(oxypropylene) glycols in the molar mass range M_n from 400 to 3000.

Polyesterdiols are prepared by esterifying organic dicarboxylic acids or their anhydrides with organic
10 diols or are derived from a hydroxy carboxylic acid or from a lactone. In order to prepare branched polyesterpolyols it is possible to employ, to a minor extent, polyols or polycarboxylic acids having a higher functionality. The dicarboxylic acids and diols can be
15 linear or branched, aliphatic, cycloaliphatic or aromatic dicarboxylic acids or diols.

The diols used to prepare the polyesters consist, for example, of alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and other diols, such as
20 dimethylolcyclohexane. However, it is also possible to add small amounts of polyols, such as trimethylolpropane, glycerol, pentaerythritol.

The acid component of the polyester consists primarily of low molecular mass dicarboxylic acids or their anhydrides having 2 to 44, preferably 4 to 36 carbon atoms in the molecule. Examples of suitable acids are

5 o-phthalic, isophthalic, terephthalic, tetrahydrophthalic, cyclohexanedicarboxylic, succinic, adipic, azelaic, sebacic, maleic, fumaric, glutaric, hexachloroheptanedicarboxylic and tetrachlorophthalic acid and/or dimerized fatty acids. Instead of these

10 acids it is also possible to use their anhydrides where they exist. In the formation of polyesterpolyols it is also possible for relatively small amounts of carboxylic acids having three or more carboxyl groups to be present, examples being trimellitic anhydride or

15 the adduct of maleic anhydride with unsaturated fatty acids.

It is also possible to employ polyesterdiols which are obtained by reacting a lactone with a diol. A feature

20 of these is the presence of terminal hydroxyl groups and repeating polyester units of the formula $(-\text{CO}-(\text{CHR}^2)_n-\text{CH}_2-\text{O})$. In this formula n is preferably 4 to 6 and the substituent $\text{R}^2 =$ hydrogen, an alkyl, cycloalkyl or alkoxy radical. No substituent contains

25 more than 12 carbon atoms. The total number of carbon atoms in the substituent does not exceed 12 per lactone

ring. Examples of such compounds are hydroxycaproic, hydroxybutyric, hydroxydecanoic and/or hydroxystearic acid.

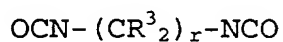
5 For preparing the polyesterdiols preference is given to the unsubstituted ϵ -caprolactone, in which n has the value 4 and all substituents R^2 are hydrogen. The reaction with lactone is initiated by low molecular mass polyols such as ethylene glycol, 1,3-propanediol, 10 1,4-butanediol, dimethylolcyclohexane. It is also possible, however, to react other reaction components, such as ethylenediamine, alkyldialkanolamines or else urea, with caprolactone. Other diols of relatively high molecular mass are polylactamdiols, which are prepared 15 by reacting, for example, ϵ -caprolactam with low molecular mass diols.

If it is intended to introduce polymerizable double bonds into the polyurethane molecules by way of 20 component (a), then it is necessary to employ components (a) which contain polymerizable double bonds. Examples of such components (a) are polyesterpolyols, preferably polyesterdiols, which have been prepared using polyols and/or polycarboxylic acids 25 containing polymerizable double bonds. Examples of polyols containing polymerizable double bonds are:

trimethylolpropane monoallyl ether, glycerol monoallyl ether, pentaerythritol mono- and diallyl ether. Examples of polycarboxylic acids containing polymerizable double bonds are alkenedicarboxylic acids, maleic acid and unsaturated dimerized fatty acids.

As component (b) it is possible to employ aliphatic and/or cycloaliphatic and/or aromatic polyisocyanates. Examples of aromatic polyisocyanates are phenylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, biphenylene diisocyanate, naphthylene diisocyanate and diphenylmethane diisocyanate.

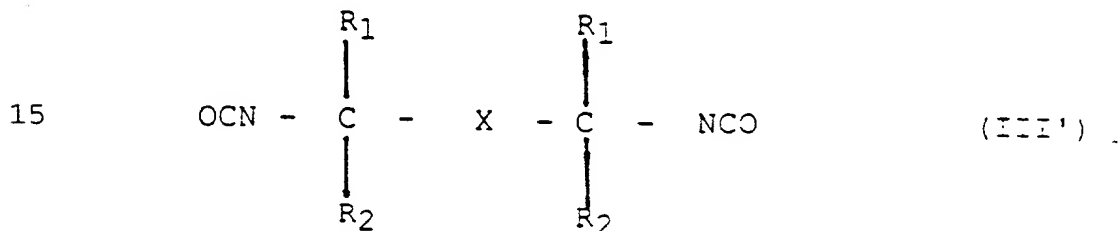
Because of their good resistance to ultraviolet light, (cyclo)aliphatic polyisocyanates give rise to products having a low tendency towards yellowing. Examples of cycloaliphatic polyisocyanates are isophorone diisocyanate, cyclopentylene diisocyanate and also the hydrogenation products of the aromatic diisocyanates, such as cyclohexylene diisocyanate, methylcyclohexylene diisocyanate and dicyclohexylmethane diisocyanate. Aliphatic diisocyanates are compounds of the formula



in which r is an integer from 2 to 20, in particular from 6 to 8 and R^3 , which can be identical or

different, is hydrogen or a lower alkyl radical having
1 to 8 C atoms, preferably 1 or 2 C atoms. Examples
thereof are trimethylene diisocyanate, tetramethylene
diisocyanate, pentamethylene diisocyanate,
5 hexamethylene diisocyanate, propylene diisocyanate,
ethylethylene diisocyanate, dimethylethylene
diisocyanate, methyltrimethylene diisocyanate and
trimethylhexane diisocyanate.

10 Further examples of suitable diisocyanates are
diisocyanates of the general formula (III')



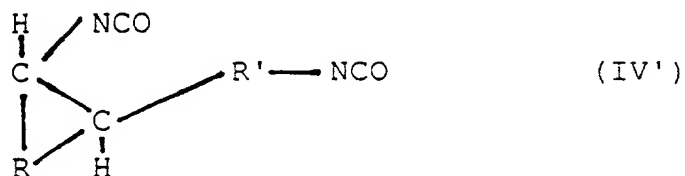
where X is a divalent, aromatic hydrocarbon radical,
preferably an unsubstituted or halogen-, methyl- or
20 methoxy-substituted naphthylene, diphenylene or 1,2-,
1,3- or 1,4-phenylene radical, with particular
preference a 1,3-phenylene radical and R₁ and R₂ are an
alkyl radical having 1 - 4 C atoms, preferably a methyl
radical. Diisocyanates of the formula (III') are known
25 (their preparation is described, for example, in EP-A-
101 832, US-A-3,290,350, US-A-4,130,577 and US-A-

4,439,616) and some are obtainable commercially; (1,3-bis(2-isocyanatoprop-2-yl)benzene, for example, is sold by the American Cyanamid Company under the trade name TMXDI (META)®).

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Also suitable as the diisocyanate component are diisocyanates of the formula (IV')

10



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where R is a divalent alkyl or aralkyl radical having 3 to 20 carbon atoms and R' is a divalent alkyl or aralkyl radical having 1 to 20 carbon atoms.

Particularly preferred diisocyanates are isophorone diisocyanate and dicyclohexylmethane diisocyanate.

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The composition of components (b) in terms of the functionality of the polyisocyanates must be such that no crosslinked polyurethane resin is obtained. In addition to diisocyanates, component (b) may also include a proportion of polyisocyanates having functionalities of more than two - such as triisocyanates, for example.

25

Products which have been found suitable as triisocyanates are those formed by trimerization or oligomerization of diisocyanates or by reaction of diisocyanates with polyfunctional OH- or NH-containing
5 compounds. Examples of these include the biuret of hexamethylene diisocyanate and water, the isocyanurate of hexamethylene diisocyanate, or the adduct of isophorone diisocyanate with trimethylolpropane. The average functionality can be lowered if required by
10 adding monoisocyanates. Examples of such chain-terminating monoisocyanates are phenyl isocyanate, cyclohexyl isocyanate and stearyl isocyanate.

Component (c) serves to introduce polymerizable double
15 bonds into the polyurethane resin molecules. It is preferred as component (c) to employ a compound which contains at least two NCO-reactive groups and one polymerizable double bond. Particular preference is given to the use, as component (c), of compounds which
20 in addition to a polymerizable double bond also contain two NCO-reactive groups. Examples of NCO-reactive groups are -OH, -SH, >NH and -NH₂ groups, preference being given to -OH, >NH and -NH₂ groups.

25 Examples of compounds which can be employed as component (c) are: hydroxy (meth)acrylates, especially

hydroxyalkyl (meth)acrylates such as hydroxyethyl, hydroxypropyl, hydroxybutyl or hydroxyhexyl (meth)-acrylate and 2,3-dihydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl monoallyl ether, allyl 2,3-dihydroxy-
5 propanoate, glycerol mono(meth)acrylate, glycerol monoallyl ether, pentaerythritol mono(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol monoallyl ether, pentaerythritol diallyl ether, trimethylolpropane monoallyl ether, trimethylpropane
10 mono(meth)acrylate and trimethylolpropane diallyl ether. As component (c) it is preferred to employ trimethylolpropane monoallyl ether, glycerol mono(meth)acrylate, allyl 2,3-dihydroxypropanoate, pentaerythritol di(meth)acrylate, pentaerythritol
15 diallyl ether, glycerol monoallyl ether and trimethylolpropane mono(meth)acrylate. It is preferred to incorporate the components (c) which contain at least two NCO-reactive groups into the polyurethane molecules at sites within the chain (not at the end).

20

The introduction into the polyurethane molecules of groups capable of forming anions takes place by way of the incorporation into the polyurethane molecules of compounds (d) whose molecule contains at least one
25 isocyanate-reactive group and one group capable of forming anions.

The amount of component (d) to be employed can be calculated from the target acid number.

- 5 As component (d) it is preferred to employ compounds whose molecule contains two isocyanate-reactive groups. Suitable isocyanate-reactive groups are, in particular, hydroxyl groups, and also primary and/or secondary amino groups. Suitable groups capable of forming anions
10 are carboxyl groups, sulphonic acid groups and/or phosphonic acid groups, with preference being given to carboxyl groups. As component (d) it is possible, for example to employ alkanolic acids having two substituents on the α carbon atom. The substituent can
15 be a hydroxyl group, an alkyl group or, preferably, an alkylol group. These alkanolic acids have at least one, generally 1 to 3, carboxyl groups in the molecule. They have from two to about 25, preferably from 3 to 10 carbon atoms. Examples of component (d) are
20 dihydroxypropionic acid, dihydroxysuccinic acid and dihydroxybenzoic acid. A particularly preferred group of alkanolic acids are the α,α -dimethylolalkanoic acids of the general formula

where R^4 is a hydrogen atom or an alkyl group having up to about 20 carbon atoms.

Examples of such compounds are 2,2-dimethylolacetic acid, 2,2-dimethylolpropionic acid, 2,2-dimethylolbutyric acid and 2,2-dimethylolpentanoic acid. The preferred dihydroxyalkanoic acid is 2,2-dimethylolpropionic acid. Amino-containing compounds are, for example, α,δ -diaminovaleric acid, 3,4-diaminobenzoic acid, 2,4-diaminotoluenesulphonic acid and 2,4-diamino-diphenyl ether sulphonic acid.

With the aid of component (e) it is possible to introduce poly(oxyalkylene) groups as nonionic stabilizing groups into the polyurethane molecules. As component (e) it is possible, for example, to employ alkoxypoly(oxyalkylene) alcohols having the general formula $R'O-(-CH_2-CHR''-O-)_nH$, in which R' is an alkyl radical having 1 to 6 carbon atoms, R'' is a hydrogen atom or an alkyl radical having 1 to 6 carbon atoms and n is a number between 20 and 75.

The use of component (f) leads to an increase in the molecular weight of the polyurethane resins. As component (f) it is possible, for example, to employ polyols having up to 36 carbon atoms per molecule, such

as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,2-butylene glycol, 1,6-hexanediol, trimethylolpropane, castor oil or hydrogenated castor oil, ditrimethylolpropane ether, pentaerythritol, 1,2-cyclohexanediol, 1,4-cyclohexanedimethanol, bisphenol A, bisphenol F, neopentyl glycol, neopentyl glycol hydroxypivalate, hydroxyethylated or hydroxypropylated bisphenol A, hydrogenated bisphenol A and mixtures thereof. The polyols are generally employed in amounts of up to 30 per cent by weight, preferably from 2 to 20 per cent by weight, based on the amount of component (a) and (f) employed.

As component (f) it is also possible to employ di- and/or polyamines having primary and/or secondary amino groups. Polyamines are essentially alkylene-polyamines having 1-40 carbon atoms, preferably about 2 to 15 carbon atoms. They may carry substituents which do not have any isocyanate-reactive hydrogen atoms. Examples are polyamines with a linear or branched aliphatic, cycloaliphatic or aromatic structure and at least two primary amino groups. Diamines which can be mentioned are hydrazine, ethylenediamine, propylenediamine, 1,4-butylenediamine, piperazine, 1,4-cyclohexyldimethylamine, 1,6-hexamethylenediamine, trimethylhexamethylen-

diamine, menthanediamine, isophoronediamine, 4,4'-
diaminodicyclohexylmethane and aminoethylethanolamine.
Preferred diamines are hydrazine, alkyl- or
cycloalkyldiamines such as propylenediamine and 1-
5 amino-3-aminomethyl-3,5,5-trimethylcyclohexane. It is
also possible to employ as component (f) polyamines
which contain more than two amino groups in the
molecule. In such cases, however, care should be taken
- for example by using monoamines as well - that no
10 crosslinked polyurethane resins are obtained. Such
polyamines which can be used are diethylenetriamine,
triethylenetetramine, dipropylenediamine and dibuty-
lenetriamine. Ethylhexylamine is given as an example of
a monoamine.

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The binders employed in accordance with the invention
are prepared by preparing a solution of polyurethane
resin (B) in an organic solvent or an organic solvent
mixture and, in this solution, polymerizing
20 ethylenically unsaturated monomers or a mixture of
ethylenically unsaturated monomers in a free-radical
polymerization, and converting the resulting reaction
product into an aqueous dispersion. It is preferred to
employ water-miscible organic solvents. Examples of
25 solvents which can be used are butylglycol, 2-
methoxypropanol, n-butanol, methoxybutanol, n-propanol,

ethylene glycol monomethyl ether, ethylene glycol
monoethyl ether, ethylene glycol monobutyl ether,
diethylene glycol monomethyl ether, diethylene glycol
monoethyl ether, diethylene glycol diethyl ether,
5 diethylene glycol monobutyl ether and 3-methyl-3-
methoxybutanol or mixtures of these solvents.

Preference is given to ketones, such as acetone, methyl
ethyl ketone, diethyl ketone and methyl isobutyl
10 ketone, for example.

The free-radical polymerization is conducted at
temperatures from 80 to 160°C, preferably from 100 to
160°C, in the abovementioned organic solvents or
15 solvent mixtures, if desired under superatmospheric
pressure.

Examples of polymerization initiators which can be used
are initiators which form free radicals, such as
20 benzoyl peroxide, azobisisobutyronitrile, t-butyl
perethylhexanoate and t-butyl perbenzoate, for example.

In the course of the polymerization there are also
grafting reactions between the polyurethane resin (B)
25 and component (A). The components (A) and (B) are
employed in a weight ratio of from 1 : 10 to 10 : 1,

preferably from 1 : 2 to 2 : 1, and, with particular preference, from 1 : 1.

Ethylenically unsaturated monomers which can be
5 employed are virtually all free-radically polymerizable
monomers but subject to the usual restrictions for
copolymerizations as defined by the Q and e scheme of
Alfrey and Price and/or by the copolymerization
parameters (cf. e.g. Brandrup and Immergut, Polymer
10 Handbook, 2nd ed. John Wiley & Sons, New York (1975)).

Ethylenically unsaturated monomers which can be
employed are:

15 (i) aliphatic or cycloaliphatic esters of acrylic acid
or methacrylic acid or a mixture of such esters, and

(ii) ethylenically unsaturated monomers which carry at
least one hydroxyl group in the molecule, or a mixture
20 of such monomers, and

(iii) ethylenically unsaturated monomers which carry at
least one carboxyl group in the molecule or a mixture
of such monomers, and

- (iv) ethylenically unsaturated monomers other than (i),
(ii) and (iii), or a mixture of such monomers, and also
(v) polyunsaturated monomers, especially ethylenically
5 polyunsaturated monomers.

The abovementioned monomers are preferably employed as
mixtures, in which component (i) is employed in an
amount of from 40 to 100, preferably from 60 to 90 % by
10 weight, component (ii) in an amount of from 0 to 20,
preferably from 3 to 12 % by weight, component (iii) in
an amount of from 0 to 30, preferably from 5 to 15 % by
weight, component (iv) in an amount of from 0 to 30,
preferably from 0 to 10 % by weight and component (v)
15 in an amount of from 0 to 5, preferably 0 % by weight,
the sum of the proportions by weight of (i), (ii),
(iii), (iv) and (v) always being 100 % by weight.

As component (i) it is possible, for example, to
20 employ: cyclohexyl acrylate, cyclohexyl methacrylate,
aklyl acrylate and alkyl methacrylates having up to 20
carbon atoms in the alkyl radical, such as methyl,
ethyl, propyl, butyl, hexyl, ethylhexyl, stearyl and
lauryl acrylate and methacrylate or mixtures of these
25 monomers.

As component (ii) it is possible, for example, to employ: hydroxyalkyl esters of acrylic acid, methacrylic acid or another α,β -ethylenically unsaturated carboxylic acid. These esters can be
5 derived from an alkylene glycol which is esterified with the acid, or they can be obtained by reacting the acid with an alkylene oxide. As component (ii) it is preferred to employ hydroxyalkyl esters of acrylic and methacrylic acid in which the hydroxyalkyl group
10 contains up to 4 carbon atoms, or mixtures of these hydroxyalkyl esters. Examples of such hydroxyalkyl esters are 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 2-hydroxyethyl
15 methacrylate, 3-hydroxybutyl acrylate or 4-hydroxybutyl (meth)acrylate. Corresponding esters of other unsaturated acids, such as ethacrylic acid, crotonic acid and similar acids having up to about 6 carbon atoms per molecule, can also be employed.

20

As component (iii) it is preferred to employ acrylic acid and/or methacrylic acid. It is also possible, however, to employ other ethylenically unsaturated acids having up to 6 carbon atoms in the molecule.
25 Examples of such acids are ethacrylic, crotonic, maleic, fumaric and itaconic acid.

As component (iv) it is possible, for example, to employ: vinylaromatic hydrocarbons, such as styrene, α -alkylstyrene and vinyltoluene, acryl- and
5 methacrylamide and acryl- and methacrylonitrile or mixtures of these monomers.

Compounds which can be employed as components (v) are those containing at least two free-radically
10 polymerizable double bonds in the molecule. Examples are: divinylbenzene, p-methyldivinylbenzene, o-nonyl-divinylbenzene, ethanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate,
15 pentaerythritol di(meth)acrylate, allyl methacrylate, diallyl phthalate, butanediol divinyl ether, divinylethyleneurea, divinylpropyleneurea, diallyl maleate, etc.

20 Preference is given to the use of difunctional unsaturated monomers such as butanediol diacrylate or hexanediol diacrylate. If glycidyl methacrylate and methacrylic acid are used the corresponding glycerol dimethacrylate is formed automatically in the course of
25 polymerization. The nature and amount of polyunsaturated monomers should be matched carefully to

the reaction conditions (catalysts, reaction temperature, solvents) so that no gelling is obtained. The amount of polyunsaturated monomers added serves to raise the mean molar mass without gelling. However, it is preferred to add no polyunsaturated monomer.

The polymers (P) prepared from (A) and (B) and employed in accordance with the invention must contain groups which are capable of forming anions, which are neutralized before or during the transfer of the polymers from the organic solvent or solvent mixture into water and which allow the formation of stable aqueous dispersions. The polymers concerned may in addition to the groups capable of forming anions also contain nonionic stabilizing groups such as, for example, poly(oxyalkylene) groups, especially poly(oxyethylene) and/or poly(oxypropylene) and/or poly(oxyethylene)(oxypropylene) groups.

The amount of groups capable of forming anions present in the polymers (P) which are employed in accordance with the invention and are prepared from (A) and (B) should be sufficiently high for the polymers to have an acid number of from 5 to 200, preferably from 10 to 40, and, with particular preference, from 15 to 30. The introduction of the groups capable of forming anions

into the polymers concerned can take place, for example, by way of components (d) and (iii). The groups capable of forming anions can be present exclusively in component (A) or exclusively in component (B) or both in component (A) and in component (B). It is preferred for from 50 to 100, preferably from 70 to 100 and, with particular preference, 100 % of the groups capable of forming anions to be present in component (A).

10 The introduction of poly(oxyalkylene) groups into the polymers of the invention can take place by way of component (e) or by way of ethylenically unsaturated monomers which contain at least one poly(oxyalkylene) group (e.g. poly(oxyethylene) (meth)acrylates). The
15 polymers of the invention should not contain excessive amounts of poly(oxyalkylene) groups, since otherwise the moisture resistance of the paint films may be reduced. The content of poly(oxyalkylene) groups can be from 1 to 10 % by weight, preferably from 1 to 5 % by
20 weight (based on the weight of the polymer prepared from (A) and (B)).

The polymers (P) prepared from (A) and (B) and employed in accordance with the invention should preferably
25 contain no nonionic stabilizing groups.

The polymers (P) prepared from (A) and (B) should preferably have a hydroxyl number of from 0 to 100, with particular preference from 20 to 80. The number-average molecular weight of the polymers should
5 preferably be from 2000 to 20,000, with particular preference from 5000 to 12,000.

Particularly preferred polymers (P) are the polymers prepared from (A) and (B) which have a polymolecularity
10 index Q of from 5 to 90, preferably from 5 to 30. The polymolecularity index is the quotient $M_w : M_n$, where M_w is the weight-average and M_n the number-average molecular weight.

15 The polymolecularity (or polydispersity) index can be influenced, for example, by controlled use of regulators and by the nature of the solvents employed. Q is also influenced by the content of polymerizable double bonds in component (B). Q becomes larger the
20 smaller the amount of regulator employed and the smaller the amount of solvents employed which can function as regulators. The lower the content of polymerizable double bonds in component (B), the greater Q. Q can be determined by gel permeation
25 chromatography using a polystyrene standard.

After the end of the polymerization of component (A), the resulting polymer is at least partly neutralized and is dispersed in water.

- 5 Neutralization can be effected using both organic bases and inorganic bases, such as ammonia and hydrazine. It is preferred to use primary, secondary and tertiary amines, such as ethylamine, propylamine, dimethylamine, dibutylamine, cyclohexylamine, benzylamine, morpholine, 10 piperidine and triethanolamine, for example. Particular preference is given to the use of tertiary amines as neutralizing agents, especially dimethylethanolamine, triethylamine, tripropylamine and tributylamine.
- 15 Some or, preferably, all of the organic solvents can be distilled off if desired from the aqueous binder dispersions obtained. The binder dispersions comprise polymer particles whose average size lies between 10 and 500 nm, preferably between 60 and 150 nm 20 (measurement method: laser light scattering, instrument: Malvern Autosizer 2 C).

It is essential to the invention that the pigment pastes have a very high pigment content. In this 25 context, however, the respective level of pigmentation depends on the particular type of pigment. For example,

pigment pastes containing carbon black are highly pigmented even at a carbon black content of more than 8 % by weight, since for carbon black the usual level of pigmentation is about 5 - 6 % by weight, based in each case on the overall weight of the pigment paste. Organic pigments, on the other hand, are employed in opaque paints, for example, in an amount of in general about 20 % by weight, and inorganic pigments (with the exception of titanium dioxide) usually in an amount of about 30 % by weight (titanium dioxide in general up to 50 % by weight), based in each case on the overall weight of the pigment paste. The pigment pastes of the invention comprise the pigments in amounts markedly higher than these. It is possible, preferably, to operate with a level of pigmentation in the vicinity of the critical pigment volume concentration (c.p.v.c.). The level of pigmentation, consequently, is preferably in general from about 3 to 10 %, with particular preference from 5 to 7 %, below the c.p.v.c. This c.p.v.c. is the amount of incorporated pigment at which the pigment is no longer wetted by the grinding medium. The c.p.v.c. is determined experimentally.

The present invention therefore has as its subject pigment pastes which comprise

(Pa) from 10 to 35 % by weight, preferably from 15 to 25 % by weight, of at least one polyurethane acrylate resin (P), based on the solids content,

5

(Pb) from 10 to 65 % by weight, preferably from 20 to 50 % by weight, of water and

10

(Pc1) from 18 to 40 % by weight, preferably from 24 to 35 % by weight, of at least one organic, transparent pigment or from 30 to 50 % by weight, preferably from 33 to 45 % by weight, of at least one organic, opaque pigment, or

15

(Pc2) from 30 to 80 % by weight, preferably from 38 to 50 % by weight, of at least one inorganic pigment, with the exception of white pigments, or from more than 50 to 70 % by weight of white pigment, or

20

(Pc3) from more than 8 to 15 % by weight, preferably from 9 to 12 % by weight, of carbon black,

the proportions by weight of the respective components
25 (Pa) to (Pc) being based in each case on the overall

weight of the pigment paste (hence including any other components employed).

The pigment pastes can in addition - depending on shade
5 - include one or more further constituents, such as in each case, for example,

(Pd) from 0 to 10 % by weight, preferably from 3 to 8 %
by weight, of at least one dispersing auxiliary
10 and/or

(Pe) from 0 to 10 % by weight, preferably from 1 to 5 %
by weight, of one or more organic solvents and/or

15 (Pf) from 0 to 10 % by weight, preferably from 2 to 4 %
by weight, of one or more binders other than polyurethane (P) (based on solids) and/or

(Pg) from 0 to 20 % by weight, preferably from 2 to 10
20 % by weight, of one or more fillers and/or extenders and/or

(Ph) from 0 to 15 % by weight, preferably from 1 to 15
% by weight, of one or more customary auxiliaries
25 and/or additives,

the proportions by weight of components (Pd) to (Ph) again being based in each case on the overall weight of the respective pigment paste.

5 The pigment pastes of the invention preferably have a solids content of from 25 to 85 % by weight, more preferably from 40 to 70 % by weight, the respective solids content depending on the pigment type. In addition, the pigment pastes of the invention
10 preferably have a pH of from 7 to 9, with particular preference from 7.5 to 8.5 and a viscosity, at a temperature of 23°C and a shear rate of 1000 s⁻¹, of from 50 to 800 mPa.s, with particular preference from 100 to 300 mPa.s.

15 Particularly preferred pigment pastes are obtained if the pigments and the binder or binders are employed in amounts such that the pigment/binder ratio is between 5:1 and 0.5:1, with very particular preference between
20 3:1 and 2:1.

All organic and inorganic pigments are suitable in principle for use in the pigment pastes of the invention. It is possible, for example, to employ
25 various inorganic pigments, examples being black pigments such as carbon black, colour pigments,

examples being iron oxide pigments, such as red iron oxide (hematite, α -diiron trioxide), yellow iron oxide (iron oxide hydroxide) and brown iron oxide (mixed pigment of red iron oxide, yellow iron oxide and black iron oxide), and chromium oxide pigments and mixed-phase oxide pigments, and also organic pigments, such as perylenes, phthalocyanines, diketopyrrolopyrroles, isoindolinones, quinacridones, dioxazines, anthraquinones, azo pigments, diaryl pigments, indanthrones, benzimidazoles, metal complex pigments, indigo, thioindigo and the like.

The colour pigment pastes designed for solid-colour waterborne paints can also be employed in metallic paints and waterborne refinish paints. The polyurethane acrylate (P) is also suitable for the pasting up of special-effect pigments (without dispersing).

In addition, and especially in the case of critical pigments, the pigment pastes of the invention preferably also include up to 10 % by weight, with particular preference from 3 to 8 % by weight, of at least one dispersant. Suitable examples are polyalkylene oxides, especially polyoxyethylene, block copolymers having anchor groups with affinity for pigment, examples being amino groups, surfactants,

hydroxyaromatic compounds, substituted aromatic compounds, acetylenediol, mixtures of acrylates with surfactants or fatty acids, alkylphenol ethoxylates, polyurethane oligomers and the like.

5

In addition to the components (Pa) to (Pd) the pigment pastes of the invention may if desired, also include from 0 to 10 % by weight, preferably from 1 to 5 % by weight, based in each case on the overall weight of the
10 pigment paste, of one or more organic solvents (Pe). With particular preference, however, the pigment pastes are formulated essentially without solvent.

Compounds which may be mentioned as examples of
15 suitable solvents (Pe) are aliphatic or aromatic hydrocarbons, mono- or polyhydric alcohols, ethers, esters, glycol ethers and esters thereof, and ketones, examples being toluene, xylene, butanol, ethyl- or butyl glycol (= ethylene glycol monoethyl or monobutyl
20 ether) and their acetates, butyldiglycol (ethylene glycol dibutyl ether), ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, propylene glycol ether, cyclohexanone, methyl ethyl ketone, acetone, isophorone or mixtures thereof.

25

The pigment pastes of the invention may if desired also include one or more binders (Pf) other than component (Pa), preferably in an amount of from 1 to 10 % by weight, with particular preference from 2 to 4 % by weight, based in each case on the overall weight of the pigment paste and on the solids content of these binders.

Examples of suitable binders (Pf) are commonly employed aqueous grinding resins, such as polyurethanes, polyesters, polyacrylates, amino resins, polyethers and carbamates, for example.

The pigment pastes may, furthermore and if desired, include customary fillers and/or extenders (Pg), preferably in an amount of from 0 to 20 % by weight, with particular preference from 2 to 10 % by weight, based in each case on the overall weight of the pigment paste.

20

Examples of suitable fillers and/or extenders (Pg) are silicatic fillers, such as kaolin (china clay), talc, siliceous chalk, various types of mica, such as micaceous iron ore, for example, and also silicon carbide and quartz flour, carbonate-type fillers, such

as chalk and dolomite; sulphate-type fillers, such as barium and calcium sulphate, for example.

Finally, the pigment pastes may if desired also include
5 further customary auxiliaries and additives (Ph) in customary amounts, preferably in an amount of from 0 to 15 % by weight, with particular preference from 1 to 5 % by weight, based in each case on the overall weight of the pigment paste.

10

Examples that may be mentioned are stabilizers, emulsifiers, rheological auxiliaries, for example inorganic phyllosilicates, silica gels, organic cellulose ethers, poly(meth)acrylic acids, poly-
15 (meth)acrylamide, polyvinyl alcohol, associative thickeners, such as hydrophobically modified ethoxylated urethanes and the like, for example, plasticizers, such as polypropylene oxides, wetting agents, such as alkylphenol ethoxylates or
20 acetylenediols, levelling agents, such as acrylates and silicone oils, antifoams, such as silicone oil antifoams and mineral oil antifoams with solid constituents, for example, and also biocides, fungicides, etc. These substances can be added to the
25 individual components and/or to the overall mixture.

The pigment pastes are prepared by the customary methods known to the skilled worker. This usually involves predispersing the pigment or pigments and, if used, the filler or fillers and extender or extenders in a portion of the binder and then carrying out grinding to the sufficient particle size and colour strength. The make-up mixture used is the customary quantity of binder, with or without additional binders and crosslinkers, and also solvents, dispersing auxiliaries and further additives.

The present invention likewise relates to aqueous paints comprising these pigment pastes, these paints containing the pigment paste of the invention in a proportion of from 10 to 60 % by weight, preferably from 15 to 30 % by weight, based in each case on the overall weight of the aqueous paints.

The pigment pastes are employed in accordance with the present invention, preferably for preparing solid-colour basecoats, but also metallic paints and water-based refinish paints, which are suitable for the coating of metal and/or plastic substrates. The present invention therefore relates likewise to methods of coating metal and/or plastic substrates which are characterized in that aqueous paints are employed which

contain from 10 to 60 % by weight, preferably from 15 to 30 % by weight, of the above-described pigment paste and from 40 to 80 % by weight, preferably from 50 to 70 % by weight, of a customary coating composition, preferably a solid-colour basecoat composition, based in each case on the overall weight of the aqueous paint.

It is possible, furthermore, to prepare different shades of the basecoat using different pigment pastes of the invention. Also possible, therefore, is the use of the pigment pastes of the invention to construct a mixer system which can be used to produce paints having a fixed shade. Mixer systems of this kind can be used directly, for example, at the premises of the respective paint manufacturer or else at those of the respective customer, for example at the premises of the car maker in order to produce production-line automotive finishes. If the appropriate choice of the crosslinkers or grinding binders (in the sector of refinishing, for example, physically drying binders) also ensures low stoving temperatures of the paints, the pigment pastes of the invention can also be employed to prepare mixer systems in the field of automotive refinishing or of the painting of plastics.

Another subject of the invention, therefore, is a mixer system for the preparation of aqueous coating materials which is characterized in that the mixer system comprises various pigment pastes of the invention.

5

Then, to prepare the aqueous paints having the particular shade desired, one or more of the pigment pastes of the invention are mixed with one or more pigment-free components which comprise the other
10 constituents of the aqueous paints.

The aqueous paints concerned, preferably solid-colour basecoats, prepared using the pigment pastes of the invention usually include not only the pigment paste
15 but also one or more binders, preferably at least one polyurethane acrylate (P), a crosslinker, such as amino resins, blocked isocyanates, triazine-based crosslinkers, for example, possibly rheological auxiliaries, and/or other customary auxiliaries and
20 additives and also, if desired, organic solvents.

Customary coating materials or solid-colour basecoats which are combined with the pigment paste or pastes of the invention to form the paint of the invention are
25 those comprising customary commercial raw materials, such as polyesters, polyacrylates, cellulose

derivatives, preferably at least a portion of the above-described polyurethane acrylate (P), rheological auxiliaries, such as waxes, and also other auxiliaries and additives.

5

In general, the proportion of urethane acrylate (P) in such paints - depending on shade - is from 10 to 19 % by weight, preferably from 12 to 17 % by weight. The proportion of crosslinker, in the form for example of a triazine resin, is generally from 3 to 9 % by weight, preferably from 4 to 8 % by weight. The overall pigment content, depending on shade and pigment type, is generally between 5 and 30 % by weight. The water content of such coating systems is usually between 30 and 50 % by weight, while the proportion of organic solvents fluctuates in general, depending on the shade and formulation, between 5 and 20 % by weight. It is also possible, however, to produce paints which are free from cosolvent.

20

It is also possible to add crosslinked polymeric micro particles as disclosed in EP-A-38 127 to the basecoats, and/or customary inorganic or organic rheological additives in customary amounts, for example from 0.05 to 6 % by weight, based on the overall weight of the basecoat. Effective thickeners, for example, are

inorganic phyllosilicates, such as aluminium-magnesium
silicates, sodium-magnesium phyllosilicates and sodium-
magnesium-fluorine-lithium phyllosilicates of the
montmorillonite type, water-soluble cellulose ethers,
5 such as hydroxyethylcellulose, methylcellulose or
carboxymethylcellulose, and synthetic polymers having
ionic and/or associative groups, such as polyvinyl
alcohol, poly(meth)acrylamide, poly(meth)acrylic acid,
polyvinylpyrrolidone, styrene-maleic anhydride or
10 ethylene-maleic anhydride copolymers and their
derivatives, or else hydrophobically modified,
ethoxylated urethanes or polyacrylates. Also suitable
is a combination of carboxyl-containing polyacrylate
copolymer having an acid number of from 60 to 780,
15 preferably from 200 to 500 mg of KOH/g and a sodium-
magnesium phyllosilicate. The sodium-magnesium phyllo-
silicate can also be employed in the form of an aqueous
paste. Preferred pastes comprise either 3 % by weight
of phyllosilicate and 3 % by weight of polypropylene
20 glycol and 2 % by weight of phyllosilicate and 2 % by
weight, based in each case on the overall weight of the
paste, of other customary commercial surface-active
substances.

5 The basecoats may in addition include customary organic solvents. The proportion thereof will be kept as low as possible. It is, for example, below 15 % by weight.

15 Finally, the pigment pastes of the invention are also
suitable for preparing radiation-curable paints,
especially paints which are curable by means of UV
radiation or electron beams. To this end the pigment
pastes of the invention are combined with radiation-
20 curable binder solutions and/or radiation-curable
binder dispersions and also any other auxiliaries and
additives typical for radiation-curable paints. It is
surprising that no instances of incompatibility occur
here despite the fact that the pigment pastes of the
25 invention are not themselves radiation-curable and do

not comprise a radiation-curable polyurethane dispersion.

The paints of the invention prepared with the aid of
5 pigment pastes of the invention (e.g. basecoats, UV
paints and the like, see above) can be applied to a
very wide variety of substrates, such as metal,
plastic, wood or paper, for example. Application takes
place by customary methods, such as spraying, knife
10 coating, dipping or brushing, for example.

The coating materials of the invention are preferably
used to produce topcoats as part of a single-coat or
multicoat finish. The coating materials of the
15 invention can be employed, for example, for both the
production-line finishing and the refinishing of car
bodies. They are preferably employed in the field of
production-line finishing.

20 The paints of the invention are normally cured, after
initial drying and overcoating with clearcoats, at
temperatures from 80 to 160°C, preferably at
temperatures from 100 to 140°C. In specific forms of
use of the paints of the invention it is possible,
25 given an appropriate choice of crosslinkers, to employ

lower curing temperatures or to employ physically drying systems.

In the text below the invention is elucidated further
5 on the basis of working examples. In these examples,
all parts and percentages are by weight unless
expressly stated otherwise.

1. Preparing a polyurethane acrylate dispersion

10 (Component a)

In a reaction vessel with stirrer, reflux condenser and
two feed vessels 63.5 parts of isophorone diisocyanate
are added to a mixture of 77.6 parts of a polyesterdiol
having a number-average molecular weight of 630 and
15 formed from adipic acid, hexanediol and neopentyl
glycol, 9.3 parts of neopentyl glycol, 3.0 parts of
trimethylolpropane monoallyl ether, 0.1 part of
dibutyltin dilaurate and 110.2 parts of methyl isobutyl
ketone. The reaction mixture is subsequently heated to
20 105°C. At an NCO content of 1.8 %, 15.1 parts of
trimethylolpropane are added to the reaction mixture
and the reaction is continued until isocyanate groups
can no longer be detected.

25 Subsequently, at a temperature of 105°C, a mixture of
69.6 parts of n-butyl acrylate, 69.6 parts of methyl

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methacrylate, 16.6 parts of hydroxypropyl methacrylate and 13.0 parts of acrylic acid is added to the reaction mixture over the course of 3 hours. At the same time, 5.1 parts of t-butyl perethylhexanoate, dissolved in 5 42.8 parts of methyl isobutyl ketone, are metered in over the course of 3.5 hours. After a further 2.5 hours at 105°C the reaction mixture is cooled to 90°C. Then 10.6 parts of dimethylethanolamine and 483.2 parts of deionized water are added. Removal of the methyl 10 isobutyl ketone in vacuo gives a stable 43 % dispersion at a pH of 7.9.

2. Preparing pigment pastes

2.1 Preparing a pigment paste 1 containing inorganic 15 pigments

350.0 g of the above-described polyurethane acrylate dispersion are introduced into a vessel. With stirring (4 m/s) 40.0 g of deionized water and 350.0 g of a chromium titanium pigment are added. The batch is then 20 treated with a laboratory dissolver at a stirrer speed of 20 m/s for 5 minutes. During this treatment the temperature remains below 40°C. After dissolver treatment beforehand, the mixture is subjected to circulation grinding in a continuous laboratory stirrer 25 mill (grinding medium = SAZ beads; grinding medium size = 1.0 to 1.6 mm; degree of filling of the grinding

chamber = 75 % and rotor speed = 7.5 m/s). The specific energy input is 100 Wh/kg. The temperature remains below 40°C. Subsequently, the paste meets the requirements of an aqueous pigment paste which is employed in a production-line automotive finish (cf. also Table 1).

2.2 Preparing a pigment paste 2 containing organic pigments

290.0 g of the above-described polyurethane acrylate dispersion are introduced into a vessel. With stirring (4 m/s) 140.0 g of deionized water and 35.0 g of a commercial wetting and dispersing additive are added and 285.0 g of a phthalocyanine blue pigment. The batch is then treated with a laboratory dissolver at a stirrer speed of 20 m/s for 5 minutes. During this treatment the temperature remains below 40°C. After dissolver treatment beforehand, the mixture is subjected to circulation grinding in a continuous laboratory stirrer mill (grinding medium = SAZ beads; grinding medium size = 1.0 to 1.6 mm; degree of filling of the grinding chamber = 75 % and rotor speed = 7.5 m/s). The specific energy input is 460 Wh/kg. The temperature remains below 40°C. Subsequently, the paste meets the requirements of an aqueous pigment paste

which is employed in a production-line automotive finish (cf. also Table 1).

2.3 Preparing a pigment paste 3 containing white
5 pigments

350.0 g of the above-described polyurethane acrylate dispersion are introduced into a vessel. With stirring (4 m/s) 16.0 g of deionized water and 16.0 g of isopropoxypropanol are added and 415.0 g of a titanium
10 dioxide pigment. The batch is then treated with a laboratory dissolver at a stirrer speed of 20 m/s for 5 minutes. During this treatment the temperature remains below 40°C. After dissolver treatment beforehand, the mixture is subjected to circulation grinding in a
15 continuous laboratory stirrer mill (grinding medium = SAZ beads; grinding medium size = 1.0 to 1.6 mm; degree of filling of the grinding chamber = 75 % and rotor speed = 7.5 m/s). The specific energy input is 75 Wh/kg. The temperature remains below 40°C.
20 Subsequently, the paste meets the requirements of an aqueous pigment paste which is employed in a production-line automotive finish (cf. also Table 1).

Table 1: Storage stability of the pigment pastes 1 to 3

| Paste | Parameter | As-obtained value | Value after storage |
|-------|-----------------|-------------------|---------------------|
| 1 | Colour strength | 100.0 % | 97.7 % |
| 1 | Colour locus | 0.0 DE | 0.2 DE |
| 1 | Viscosity | 315 mPa.s | 422 mPa.s |
| 2 | Colour Strength | 100.0 % | 103.9 % |
| 2 | Colour locus | 0.0 DE | 0.25 DE |
| 2 | Viscosity | 300 mPa.s | 331 mPa.s |
| 3 | Whitening power | 100.0 % | 98 % |
| 3 | Colour locus | 0.0 DE | 0.12 DE |
| 3 | Viscosity | 350 mPa.s | 440 mPa.s |

Key to Table 1:

5

Colour strength: measured by colorimetry using a white blend in which the amounts of the above-described white paste 3 and the pigment paste are chosen so that there is one part of colour pigment (solids) to 10 parts of titanium dioxide (solids).

Colour locus: measured by colorimetry; the figure stated for the pigment pastes 1 and 2 is the colour locus for the pure shade, and for the pigment paste 3 the colour locus of the white reduction (1 part of

15

colour pigment, solids, to 10 parts of titanium dioxide, solids)

Viscosity: The figure stated is the viscosity at a
5 temperature of 23°C and measured at a shear rate of
1000 s⁻¹

3. Preparing a make-up mixture for preparing water-
borne paints

- 10 The apparatus is first of all cleaned by rinsing it
with solvent and deionized water. To improve
homogenization, all of the components employed to
prepare the make-up mixture are treated in a dissolver.
- 15 First of all, 21.4 parts of a solution of thixotropic
agent based on a synthetic phyllosilicate (3 % in
deionized water) are introduced and are treated for
about 10 minutes with a dissolver (maximum stirrer
speed). Then 39.0 parts of the above-described
- 20 polyurethane acrylate dispersion and then 0.6 part of a
customary commercial antifoam based on a combination of
liquid hydrocarbons, hydrophobic silica, synthetic
copolymers and nonionic emulsifiers are added. Then 3.0
parts of butyl diglycol, 1.5 parts of butyl glycol, 5.0
- 25 parts of Shellsol® T, 5.0 parts of N-methylpyrrolidone
and 2.5 parts of ethylhexanol are added. Subsequently,

5.0 parts of a customary commercial wetting agent solution based on acetylenediol (12.5 % in butyldiglycol) and 2.5 parts of polypropylene glycol are added. To adjust the pH to 7.8-8.5, 3.0 parts of a 10 % strength amine solution are added and the batch is finally adjusted with 11.5 parts of deionized water to give the desired solids content.

4. Preparing solid-colour basecoats

4.1 Preparing a white solid-colour waterborne basecoat

50.0 parts of the white paste 3 described above are introduced into a vessel and the remaining constituents, set out below, are treated in a dissolver. 44.0 parts of the above-described make-up mixture are first of all added to the white paste. Then 3.25 parts of a customary commercial melamine resin (90 % in isobutanol, commercial product Cymel 327 from Cyanamid) and 2.1 parts of a further customary commercial melamine resin (100 %, commercial product Cymel 303 from Cyanamid) are added. Then, for improved crosslinking, 0.65 part of a customary commercial catalyst solution based on para-toluenesulphonic acid (25 % in isopropanol) is added. The batch is then treated in a dissolver for 30 minutes (maximum stirrer speed).

20.0 parts of the blue paste 2 described above are introduced into a vessel and the remaining constituents, set out below, are treated in a

5 dissolver. 71.0 parts of the above-described make-up
mixture are first of all added to the blue paste. Then
9.0 parts of a customary commercial melamine resin
(90 % in isobutanol, commercial product Cymel 327 from
Cyanamid) are added. The batch is then treated in a
10 dissolver for 30 minutes (maximum stirrer speed).

Patent Claims:

1. Pigment paste which comprises as binder at least
one polyurethane acrylate (P) which is obtainable
5 by polymerizing, in an organic solvent or in a
mixture of organic solvents,

(A) ethylenically unsaturated monomers, or a
mixture of ethylenically unsaturated
10 monomers, in the presence of

(B) a polyurethane resin (B) which has a number-
average molecular weight of from 200 to
30,000, preferably from 1000 to 5000, and
15 which contains on average from 0.05 to 1.1,
preferably from 0.2 to 0.9 and, with
particular preference, from 0.3 to 0.7
polymerizable double bonds per molecule, and
converting the resulting reaction product
20 into an aqueous dispersion,

characterized in that the pigment paste comprises

(Pa) from 10 to 35 % by weight of at least
25 one polyurethane acrylate resin (P),
based on the solids content,

(Pb) from 10 to 65 % by weight of water and

(Pc1) from 18 to 40 % by weight of at least
one organic, transparent pigment or from
30 to 50 % by weight of at least one
organic, opaque pigment, or

(Pc2) from 30 to 80 % by weight of at least
one inorganic pigment, with the
exception of white pigments, or from
more than 50 to 70 % by weight of white
pigment, or

(Pc3) from more than 8 to 15 % by weight of
carbon black,

the proportions by weight of the respective
components (Pa) to (Pc) being based in each case
on the overall weight of the pigment paste.

2. Pigment paste according to Claim 1, characterized
in that it comprises

(Pa) from 15 to 25 % by weight of at least
one polyurethane acrylate resin (P),
based on the solids content,

(Pb) from 20 to 50 % by weight of water and

5 (Pc1) from 24 to 35 % by weight of at least
one organic, transparent pigment or from
33 to 45 % by weight of at least one
organic, opaque pigment, or

10 (Pc2) from 38 to 50 % by weight of at least
one inorganic pigment, with the
exception of white pigments, or

15 (Pc3) from 9 to 12 % by weight of carbon
black,

the proportions by weight of the components (Pa)
to (Pc) being based in each case on the overall
weight of the pigment paste.

20 3. Pigment paste according to Claim 1 or 2,
characterized in that it additionally comprises
one or more of the following constituents

25 (Pd) from 0 to 10 % by weight, preferably from 3
to 8 % by weight, of at least one dispersing
auxiliary and/or

(Pe) from 0 to 10 % by weight, preferably from 1 to 5 % by weight, of one or more organic solvents and/or

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(Pf) from 0 to 10 % by weight, preferably from 2 to 4 % by weight, of one or more binders other than polyurethane (P) (based on solids) and/or

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(Pg) from 0 to 20 % by weight, preferably from 2 to 10 % by weight, of one or more fillers and/or extenders and/or

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(Ph) from 0 to 15 % by weight, preferably from 1 to 15 % by weight, of one or more customary auxiliaries and/or additives,

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the proportions by weight of components (Pd) to (Ph) again being based in each case on the overall weight of the respective pigment paste.

4. Pigment paste according to one of Claims 1 to 3, characterized in that it has a solids content of from 25 to 85 % by weight, preferably from 40 to 70 % by weight, and/or a pH of from 7 to 9,

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preferably from 7.5 to 8.5, and/or a viscosity, at a temperature of 23°C and a shear rate of 1000 s⁻¹, of from 50 to 800 mPa.s, preferably from 100 to 300 mPa.s.

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5. Pigment paste according to one of Claims 1 to 4, characterized in that the pigment/binder ratio in the pigment paste is between 5:1 and 0.5:1, preferably between 3:1 and 2:1.

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6. Aqueous paint, characterized in that it comprises one or more pigment pastes according to one of Claims 1 to 5.

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7. Aqueous paint according to Claim 6, characterized in that it comprises from 10 to 60 % by weight, preferably from 15 to 30 % by weight, of at least one pigment paste according to one of Claims 1 to 5.

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8. Aqueous paint according to Claim 6 or 7, characterized in that it comprises as binder at least one polyurethane acrylate (P), alone or together with other binders.

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9. Method of coating substrates, characterized in that an aqueous paint according to one of Claims 6 to 8 is applied.
- 5 10. Method according to Claim 9, characterized in that the aqueous paint according to one of the claims is employed to prepare a topcoat finish, in particular as a solid-colour basecoat.
- 10 11. Use of the pigment pastes according to one of Claims 1 to 5 for preparing aqueous paints for the coating of car bodies, especially in the field of production-line finishing.
- 15 12. Use of the pigment pastes according to one of Claims 1 to 5 for preparing radiation-curable paints.
- 20 13. Mixer system for the preparation of aqueous coating compositions, characterized in that the mixer system comprises two or more pigment pastes according to one of Claims 1 to 5.

Universal pigment pastes and their use for preparing aqueous paints

Abstract

The present invention has as its subject pigment pastes which comprise as binder at least one polyurethane acrylate (P) that is obtainable by polymerizing

- (A) one or more ethylenically unsaturated monomers in the presence of
- (B) a polyurethane resin which has a number-average molecular weight of from 200 to 30,000 and which contains on average from 0.05 to 1.1 polymerizable double bonds per molecule, and converting the resulting reaction product into an aqueous dispersion,

characterized in that the pigment pastes comprise

- (Pa) from 10 to 35 % by weight of at least one polyurethane acrylate resin (P), based on the solids content,
- (Pb) from 10 to 65 % by weight of water and

(Pc1) from 18 to 40 % by weight of at least one organic, transparent pigment or from 30 to 50 % by weight of an organic, opaque pigment, or

(Pc2) from 30 to 80 % by weight of at least one inorganic pigment, with the exception of white pigments, or more than 50 to 70 % by weight of white pigment, or

(Pc3) more than 8 to 15 % by weight of carbon black,

the proportions by weight of the respective components (Pa) to (Pc) being based in each case on the overall weight of the pigment paste.

10 Rec'd PEX/PTO 26 FEB 2002

10/030307

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| | | |
|---|----------------------|--------------------------|
| DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63) <input type="checkbox"/> Declaration Submitted with initial Filing or <input checked="" type="checkbox"/> Declaration Submitted after initial Filing (surcharge (37 CFR 1.16 (e)) required) | Attorney Docket No. | IN -5550 |
| | First Named Inventor | Lutz-Werner GROSS et al. |
| | COMPLETE IF KNOWN | |
| | Application Number | 10/030,307 |
| | Filing Date | January 4, 2002 |
| | Group Art Unit | |
| Examiner Name | | |

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

AQUEOUS COATING SUBSTANCE, METHOD FOR ITS PRODUCTION AND ITS USE

(Title of the invention)

The specification of which:

☐ is attached hereto

☒ Was filed on 5 July 2000 as United States Application or PCT International Application Number **PCT/EP00/06286** and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35, U.S.C § 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or 365 (a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate, or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date DATE/MONTH/YEAR | Priority Not Claimed | Certified Copy Attached? | |
|-------------------------------------|---------|-------------------------------------|--------------------------|--------------------------|--------------------------|
| | | | | Yes | No |
| 199 32 497.2 | GERMANY | 12. JULY 1999 | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |
| | | | <input type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> |

Additional foreign application number are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C 119(e) of any United States provisional application(s) listed below:

| APPLICATION NUMBER(S) | FILING DATE |
|-----------------------|-------------|
| | |

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

| | |
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| DECLARATION — | Utility or Design Patent Application |
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POWER OF ATTORNEY

☒ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

| | | | |
|--|-------------------------|---|----------------|
| Name OF SOLE OR FIRST NVENTOR: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle [if any]) <u>Lutz-Werner</u> | | Family Name or Surname <u>GROSS</u> | |
| Inventor's Signature <u>Lutz-Werner Gross</u> | | Date <u>10.17.01</u> | |
| Residence: City | <u>D-45721 Haltern</u> | State | <u>Germany</u> |
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| Name OF SECOND INVENTOR: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle if any) | Ludwig | Family Name or Surname | MOORKAMP |
| Inventor's Signature | <i>[Signature]</i> | Date | 10.17.01 |
| Residence: City | D-48165 Münster | State | Germany |
| | | Country | Federal Republic of Germany |
| | | Citizenship | German |
| Mailing Address | Paul-Klee-Weg, 5 | | |
| City | D-48165 Münster | State | Germany |
| | | Zip | |

DECLARATION —

Utility or Design Patent Application

POWER OF ATTORNEY

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Name of Additional Joint Inventor, If any: ☐ A petition has been filed for this unsigned inventor

| | | | | | | | |
|---|-----------------------|---|----------------|---------|------------------------------------|-------------|---------------|
| Given Name first and middle [if any] <u>Heinz-Ulrich</u> | | Family Name or Surname <u>GRUMPE</u> | | | | | |
| Inventor's Signature <u>Heinz-Ulrich Grumpe</u> | | Date <u>07.12.01</u> | | | | | |
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| Name of Additional Joint Inventor, If any: | | <input type="checkbox"/> A petition has been filed for this unsigned inventor | |
| Given Name (first and middle (if any)) <u>Ulrich</u> | | Family Name or Surname <u>POTH</u> | |
| Inventor's Signature <i>Ulrich Poth</i> | | Date <u>Jan. 04th, 2002</u> | |
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